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XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

By Charles F. Mabery.

Presented March 12, 1884.

No. I.—ON β-BROMTETRACHLORPROPIONIC ACID.

With the hope of establishing the structure of certain bromdichloracrylic acids which I have at present under examination, I endeavored to prepare an acid of the same empirical composition by the addition of a molecule of chlorine to brompropiolic acid.*

In studying the relations of these substances toward each other under different conditions, it was found that the action of chlorine upon the melted acid was so violent that frequently it resulted in an explosion. Even at ordinary temperatures a gaseous product was freely evolved, with a disagreeable odor resembling that of phosgene.

As previous experiments had shown, in a chloroform solution of the acid the action of chlorine could easily be controlled; in fact, for some time it could not be determined whether the addition had begun, since evaporation of the chloroform left only a pasty mass which refused to crystallize. Finally, after continuing the action for several hours, a crust began to form above the solution, and soon the greater part of a crystalline addition product was deposited.

This substance proved to be sparingly soluble in cold carbonic disulphide and chloroform, more soluble in hot, and after purification it melted with decomposition at 225°. The percentage composition calculated from the results of analysis corresponds to that of bromtetrachlorpropionic acid.

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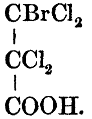
* In a former paper (Mabery and Robinson, these Proceedings, Vol. XVIII. p. 45) it was stated that a bromdichloracrylic acid could be prepared by passing chlorine through a chloroform solution of brompropiolic acid cooled to 0°. This statement was evidently made upon insufficient evidence, since all subsequent attempts to obtain the same result have proved unsuccessful.

I. 0.2000 grm. of the substance gave 0.5235 grm. AgBr + AgCl.
II. 0.5874 grm. of the substance gave 0.2732 grm. CO_2 and 0.0268 grm. H_2O.
III. 0.5385 grm. of the substance gave 0.2330 grm. CO_2.*

	Calculated for $C_3HCl_4BrO_2$.	Found. I.	II.	III.
C	12.37		12.67	11.82
H	.34		.51	
4 Cl + Br.	76.30	76.26		

The salts of this acid are extremely unstable. It dissolves readily in sodic or potassic carbonate, or in ammonic hydrate, and is precipitated by hydrochloric acid; yet the corresponding salts could not be prepared sufficiently pure for analysis. When treated with baric carbonate, the acid dissolves with the formation at first of a clear solution; but soon the latter becomes turbid from the separation of an oil, which continues until the decomposition of the salt is complete. Although this oil was not submitted to analysis, it is probably tetrachlorethylen. The silver salt which is formed when argentic nitrate is brought in contact with the acid, soon changes color, even in the dark, and all attempts to prepare it in a form suitable for analysis were unsuccessful.

Unless a molecular rearrangement takes place during the addition of chlorine, which does not seem at all probable, the structure of this acid must be represented by the formula: —



$$\begin{array}{l} CBrCl_2 \\ | \\ CCl_2 \\ | \\ COOH. \end{array}$$

Many variations of the method of preparation above described have been tried in order, if possible, to limit the addition of chlorine to the formation of a bromdichloracrylic acid. The appearance of the product and its behavior toward solvents at different stages of the chlorination would seem to indicate that each molecule of brompropiolic acid absorbed two molecules of chlorine, thereby forming a mixture of bromtetrachlorpropionic acid and unaltered brompropiolic. This would, of course, preclude the possibility of obtaining by the addition of chlorine the corresponding substituted acrylic acid.

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* By accident the water in this combustion was lost.